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For and on behalf of RWS Translations Ltd.

The 6th day of May 1994



FEDERAL REPUBLIC OF GERMANY

CERTIFICATE

Bayer Aktiengesellschaft

of

5090 Leverkusen

have filed a Patent Application under the title:

"Microbicidal Compositions"

on 5 October 1992 at the German Patent Office.

The attached document is a correct and accurate reproduction of the original submission for this Patent Application.

The German Patent Office has for the time being given the Application the symbols A 01 N 43/653 and B 27 K 3/34 of the International Patent Classification.

Munich, 19 August 1993  
President of the German Patent Office  
pp Lissner

File No: P 42 33 337.7

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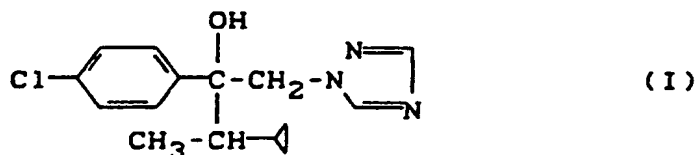
LIN/ABc

Microbicidal Compositions

The invention relates to the use of the compound  
 $\alpha$ -(4-chlorophenyl)- $\alpha$ -(1-cyclopropyl-ethyl)-  
1H-1,2,4-triazole-1-ethanol (cyproconazole) as a microbio-  
cide for the protection of industrial materials, and to  
5 synergistic mixtures containing this compound.

It has been disclosed that the azole derivatives  
described in DE-OS (German Published Specification)  
3,406,993 can be used for protecting plants.

The present invention relates to the use of an azole  
10 derivative of the formula (I)



its metal salts or acid addition compounds as a microbio-  
cide for the protection of industrial materials.

The azole derivate can not only be in the form of the  
15 free base but also in the form of a metal salt complex or  
an acid addition salt. Suitable metal salts are prefer-  
ably salts of metals of main groups II to IV and sub-  
groups I and II as well as IV to VII of the periodic  
table, the following being mentioned by way of example:  
20 copper, zinc, manganese, magnesium, tin, iron, calcium,

aluminium, lead, chromium, cobalt and nickel.

Suitable anions of the salts are those which are derived, preferably, from the following acids: hydrohalic acids such as, for example, hydrochloric acid and hydrobromic acid, furthermore phosphoric acid, nitric acid and sulphuric acid.

The metal salt complexes of the azole derivative can be obtained in a simple manner by customary processes, for example by dissolving the metal salt in alcohol, for example ethanol, and adding the solution to the azole fungicide. Metal salt complexes can be isolated in a known manner, for example by filtration, and, if appropriate, purified by recrystallisation.

The following acids are preferably suitable for preparing acid addition salts of the azole derivative: the hydrohalic acids, such as, for example, hydrochloric acid and hydrobromic acid, in particular hydrochloric acid, furthermore phosphoric acid, nitric acid, sulphuric acid, mono- and bifunctional carboxylic acids and hydroxycarboxylic acids such as, for example, acetic acid, propionic acid, 2-ethylhexanoic acid, butyric acid, mandelic acid, oxalic acid, succinic acid, 2-hydroxy-ethanedicarboxylic acid, maleic acid, fumaric acid, tartaric acid, citric acid, salicylic acid, sorbic acid, lactic acid, as well as sulphonic acids, such as, for example, p-toluenesulphonic acid, 1,4-naphthalenedisulphonic acid, alkanesulphonic acids, benzoic acid and optionally

substituted benzoic acids.

5 The acid addition salts of the compounds can be obtained in a simple manner by customary salt formation methods, for example by dissolving a compound in a suitable inert solvent and adding the acid, for example, hydrochloric acid, and they can be isolated in a known manner, for example by filtration, and, if appropriate, purified by washing with an inert organic solvent.

10 The compound (R\*, R\*)- $\alpha$ -(4-chlorophenyl)- $\alpha$ -(1-cyclopropylethyl)-1H-1,2,4-triazole-1-ethanol (cyproconazole) is particularly preferred.

15 Surprisingly, these compounds display a particularly powerful microbicidal, in particular fungicidal, activity against microorganisms which are relevant in the protection of materials, combined with a broad spectrum of action; they are active, above all, against moulds and wood-discolouring and wood-destroying fungi. The following groups of microorganisms may be mentioned by way of example, but without imposing any limitation:

20 A: Wood-discolouring fungi:

A1: Ascomycetes;

Ceratocystis such as Ceratocystis minor

A2: Deuteromycetes;

Aspergillus such as Aspergillus niger

25 Aureobasidium such as Aureobasidium pullulans

- 5           Dactylium such as Dactylium fusarioides  
           Penicillium such as Penicillium brevicaulis or  
           Penicillium variabile  
           Sclerophoma such as Sclerophoma pithyophila  
           Scopularia such as Scopularia phycomyces  
           Trichoderma such as Trichoderma viride or  
           Trichoderma lignorum
- A3: Zygomycetes:  
      Mucor such as Mucor spinosus
- 10       B: Wood-destroying fungi:
- B1: Ascomycetes:  
              Chaetomium such as Chaetomium globosum or  
              Chaetomium alba-arenulum  
              Humicola such as Humicola grisea  
 15        Petriella such as Petriella setifera  
              Trichurus such as Trichurus spiralis
- B2: Basidiomycetes  
              Coniophora such as Coniophora puteana  
              Coriolus such as Coriolus versicolor  
 20        Donkioporia such as Donkioporia expansa  
              Glenospora such as Glenospora graphii  
              Gloeophyllum such as Gloeophyllum abietinum or  
              Gloeophyllum adustum or Gl. protactum or  
              Gloeophyllum sepiarium or Gl. trabeum  
 25        Lentinus such as Lentinus cyathiformes or  
              Lentinus edodes or Lentinus lepideus or

- 5                   Lentinus grinus or L. squarrolous  
                  Paxillus such as Paxillus panuoides  
                  Pleurotus such as Pleurotis ostreatus  
                  Poria such as Poria monticola or Poria placenta  
                  or Poria vaillantii or Poria vaporaria  
                  Serpula such as Serpula himantoides or Serpula  
                  lacrymans  
                  Stereum such as Stereum hirsutum  
                  Tyromyces such as Tyromyces palustris
- 10                B3: Deuteromycetes  
                  Alternaria such as Alternaria tenuis  
                  Cladosporium such as Cladosporium herbarum

15                The amount of active substance employed depends on the  
                  species and the occurrence of the microorganisms, the  
                  microbial count and the medium. The optimum dosage rate  
                  for use can be determined in each case by test series. In  
                  general, however, it suffices to employ 0.001 to 20 % by  
                  weight, preferably 0.05 to 10 % by weight, of the active  
                  compound based on the material to be protected.

20                The active compound can be used as such, in the form of  
                  concentrates or generally customary formulations such as  
                  powder, granules, solutions, suspensions, emulsions or  
                  pastes.

25                The abovementioned formulations can be prepared in a  
                  manner known per se, for example by mixing the active  
                  compound with at least one solvent or diluent,



emulsifier, dispersant and/or binder or fixative, water repellent, optionally siccatives and UV stabilisers, and optionally colourants and pigments as well as other processing auxiliaries.

5        Suitable solvents or diluents are organochemical solvents  
or solvent mixtures and/or a polar organic solvent or  
solvent mixture and/or an oily or oil-type organochemical  
solvent or solvent mixture and/or water, if appropriate  
together with an emulsifier and/or wetting composition.  
10       Customary water-insoluble oily or oil-type solvents of  
low volatility which are preferably used are the  
particular mineral oils/mineral-oil-containing solvent  
mixtures or their aromatic fractions. White spirit,  
petroleum or alkylbenzenes, and additionally spindle oil  
15       and monochloronaphthalene may be mentioned as being  
preferred. The boiling ranges of these solvent (mixtures)  
of low volatility cover a range of approximately 170°C to  
not more than 350°C.

20       The above-described oily or oil-type solvents of low  
volatility can be replaced partially by more volatile  
organochemical solvents.

25       To prepare a wood preservative, some of the above des-  
cribed solvent or solvent mixture is preferably replaced  
by a polar organochemical solvent or solvent mixture.  
Solvents which are preferably used are those containing  
hydroxyl groups, ester groups, ether groups or mixtures  
of this functionality. Examples which may be mentioned

are esters or glycol ethers. Binders are to be understood according to the invention as being synthetic resins, binding drying oils, for example based on acrylic resins, vinyl resins, polyester resins, polyurethane resins, alkyd resins, phenol resins, hydrocarbon resins or silicone resins which can be diluted with water or are soluble, dispersible or emulsifiable in organochemical solvents. The binder used can be employed as a solution, emulsion or dispersion. Mixtures of alkyd resins and drying vegetable oil are preferably used. Alkyd resins with an oil content of between 45 and 70 % are particularly preferred.

All or some of the abovementioned binder can be replaced by a fixative (mixture) or a plasticiser (mixture). These additives are intended to prevent volatilisation of the active compound as well as crystallisation or precipitation. They preferably replace 0.01 to 30 % of the binder (based on 100 % of the binder used).

The plasticisers are from the chemical classes of the phthalic esters such as dibutyl, dioctyl or benzyl butyl phthalate, phosphoric esters such as tributyl phosphate, adipic esters such as di-(2-ethylhexyl) adipate, stearates such as butyl stearate and amyl stearate, oleates such as butyl oleate, glycerol ethers or higher-molecular-weight glycol ethers, glycerol esters as well as p-toluenesulphonic esters.

Fixatives are based, from the chemical point of view, on

polyvinyl alkyl ethers such as, for example, polyvinyl methyl ether, or ketones such as benzophenone or ethylenebenzophenone.

5 The preferred solvent or diluent is water, if appropriate in a mixture with one or more of the abovementioned solvents or diluents, emulsifiers and dispersants.

10 Industrial materials according to the invention are non-live materials which have been prepared for use in industry. For example, industrial materials which are intended to be protected by the active compound from microbial change or destruction can be glues, sizes, paper and board, textiles, leather, wood, paints and plastic articles, cooling lubricants and other materials which can be infested with, or decomposed by, micro-organisms. Parts of production plants, for example cooling-water circuits, which may be impaired by the multiplication of microorganisms may also be mentioned from amongst the materials to be protected. Preferred industrial materials beyond the scope of the invention are glues, sizes, paper and board, leather, wood, derived timber products, paints, cooling lubricants, aqueous hydraulic fluids and cooling circuits.

25 The active compound of the formula (I), or compositions or concentrates containing it, are preferably employed for protecting wood and derived timber products against microorganisms, for example against wood-destroying or wood-discolouring fungi, in particular in the protection

of tropical wood.

5 Wood which can be protected by the active compound of the  
formula (I) or by mixtures containing them is to be  
understood as meaning, for example, structural timber,  
10 wooden beams, railway sleepers, components of bridges,  
jetties, vehicles made of wood, boxes, pallets,  
containers, telegraph poles, wooden fences, wooden  
lagging, windows and doors made of wood, plywood,  
chipboard, joinery, or wooden products which are used,  
15 quite generally, for building houses or in building  
joinery.

The protection of wood is particularly effective when  
large-scale impregnating treatments, for example vacuum,  
double vacuum or pressure treatments, are used.

15 The active compound of the formula (I) is preferably  
mixed with at least one other antimicrobially active  
substance, fungicide and, in particular, with other  
active compounds, to increase the spectrum of action or  
to achieve particular effects such as, for example, an  
20 additional protection against insects. In many cases,  
this results in synergistic effect, that is to say, the  
activity of the mixture is greater than the activity of  
the individual components. Particularly preferred com-  
ponents for the mixtures are, for example, the following  
25 compounds:

Sulphenamides, such as dichlofluanid, tolylfluanid,

- folpet and fluorfolpet;
- Benzimidazoles, such as carbendazim, benomyl, fuberidazole, thiabendazole or their salts;
- 5 Thiocyanates such as thiocyanatomethylthiobenzothiazole or methylene bithiocyanate;
- Quarternary ammonium compounds such as benzyldimethyltetradecylammonium chloride, benzyldimethyldodecylammonium chloride or didecyldimethylammonium chloride;
- 10 Morpholine derivatives such as tridemorph, fenpropimorph or falimorph;
- Azoles such as triadimefon, triadimenol, bitertanol, tebuconazole, propiconazole, azaconazole, hexaconazole, prochloraz or bromuconazole;
- 15 2-(1-Chlorocyclopropyl)-1-(2-chlorophenyl)-3-(1,2,4-triazol-1-yl)-propan-2-ol;
- 20 Iodine derivatives such as diiodomethyl-p-tolyl sulphone, 3-iodo-2-propinyl alcohol, 4-chlorophenyl-3-iodopropargyl formal, 3-bromo-2,3-diiodo-2-propenyl ethylcarbamate, 2,3,3-triiodoallyl alcohol, 3-bromo-2,3-diiodo-2-propenyl alcohol, 3-iodo-2-propinyl-n-butyl carbamate, 3-iodo-2-propinyl n-hexylcarbamate, 3-iodo-2-propinyl cyclohexylcarbamate and 3-iodo-2-propinyl phenylcarbamate;

- Phenol derivatives such as tribromophenol, tetrachlorophenol, 3-methyl-4-chlorophenol, dichlorophen, o-phenylphenol, m-phenylphenol, p-phenylphenol or 2-benzyl-4-chlorophenol;
- 5 Bromine derivatives such as 2-bromo-2-nitro- 1,3-propanediol;
- Isothiazolinones such as N-methylisothiazolin-3-one, 5-chloro-N-methyl-isothiazolin-3-one, 4,5-dichloro-N-octylisothiazolin-3-one or N-octyl-isothiazolin-3-one;
- 10 Benzoisothiazolinones or cyclopenteneisothiazolinones;
- Pyridines such as 1-hydroxy-2-pyridinethione (and their sodium, iron, manganese and zinc salts) or tetrachloro-4-methylsulphonylpyridine;
- 15 Metal soaps such as tin naphthenate, tin octoate, tin 2-ethylhexanoate, tin oleate, tin phosphate, tin benzoate, copper naphthenate, copper octoate, copper 2-ethylhexanoate, copper oleate, copper phosphate, copper benzoate, zinc naphthenate, zinc octoate, zinc 2-ethylhexanoate, zinc oleate, zinc phosphate or zinc benzoate;
- 20 Oxides such as tributyltin oxide,  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$  or  $\text{ZnO}$ ;
- Dialkyldithiocarbamates such as sodium and zinc salts of dialkyldithiocarbamates, tetramethylthiuram disulphide;

Nitriles such as 2,4,5,6-tetrachloroisophthalodinitrile;

Benzothiazoles such as 2-mercaptobenzothiazol;

Quinolines, such as 8-hydroxyquinoline, and their copper salts;

5 Boron compounds, such as boric acid, boric esters or borax;

10 Formaldehyde and formaldehyde-releasing compounds such as benzyl alcohol mono(poly)-hemiformal, oxazolidines, hexahydro-S-triazines, N-methylolchloroacetamide or paraformaldehyde;

Tris-N-(cyclohexyldiazeniumdioxy)-aluminium, N-(cyclohexyldiazeniumdioxy)-tributyltin or potassium salts thereof, or bis-N-(cyclohexyldiazeniumdioxy)-copper.

The following are preferably added as insecticide:

15 Phosphoric esters such as azinphos-ethyl, azinphos-methyl, 1-(4-chlorophenyl)-4-(O-ethyl,S-propyl)phosphoryloxypyrazole, chloropyrifos, coumaphos, demeton, demeton-S-methyl, diazinon, dichlorvos, dimethoate, ethoprophos, etrimfos, fenitrothion, fenthion, heptenophos, parathion, parathion-methyl, phosalone, phoxim, 20 pirimiphos-ethyl, pirimiphos-methyl, profenofos, prothiofos, sulfprofos, triazophos and trichlorophon;

5 Carbamates such as aldicarb, bendiocarb, 2-(1-methyl-propyl)-phenyl methylcarbamate, butocarboxim, butoxycarboxim, carbaryl, carbofuran, carbosulfan, cloethocarb, isoprocarb, methomyl, oxamyl, pirimicarb, promecarb, propoxur and thiodicarb;

10 Organosilicon compounds, preferably dimethyl(phenyl)-silylmethyl 3-phenoybenzyl ethers, such as dimethyl-(4-ethoxyphenyl)silylmethyl 3-phenoxybenzyl ether or (dimethylphenyl)-silyl-methyl 2-phenoxy-6-pyridylmethyl ethers such as, for example, dimethyl(9-ethoxy-phenyl)-silylmethyl 2-phenoxy-6-pyridylmethyl ether or [(phenyl)-3-(3-phenoxyphenyl)-propyl](dimethyl)-silanes, such as, for example, (4-ethoxyphenyl)-[3-(4-fluoro-3-phenoxyphenyl-propyl)]dimethyl silane.

15 Pyrethroids, such as allethrin, alphas-methrin, biores-methrin, byfenthrin, cycloprothrin, cyfluthrin, decamethrin, cyhalothrin, cypermethrin, deltamethrin, alphacyano-3-phenyl-2-methylbenzyl 2,2-dimethyl-3-(2-chloro-2-trifluoro-methylvinyl)cyclopropanecarboxylate, fenpro-  
20 pathrin, fenfluthrin, fenvalerate, flucythrinate, flumethrin, fluvalinate, permethrin, resmethrin and tralomethrin;

25 Nitroimines and nitromethylenes, such as 1-[(6-chloro-3-pyridinyl)-methyl]-4,5-dihydro-N-nitro-1H-imidazol-2-amine (imidacloprid).

The mixtures, concentrates and formulations according to



the invention which have been prepared in this manner are not only active against the abovementioned fungi but also, if they contain an insecticide, against insects which destroy materials. The following insects which  
5 destroy materials may be mentioned by way of example, without imposing any limitation:

A: Dermaptera:

Sirex juvencus  
Urocerus augur  
10 Urocerus gigas  
Urucerus gigas taignus

B: Coleoptera:

Anobium punctatum  
Apate monachus  
15 Bostrychus capucins  
Chlorophores pilosus  
Dendrobium pertinex  
Dinoderus minutus  
Ernobius mollis  
20 Heterobostrychus brunneus  
Hylotrupes bajulus  
Lyctus africanus  
Lyctus brunneus  
Lyctus linearis  
25 Lyctus planicollis  
Lyctus pubescens  
Minthea rugicollis  
Priobium carpini  
Ptilinus pecticornis

Sinoxylon spec.  
Trogoxylon aequale  
Trypto dendron spec.  
Xestobium rufovillosum  
5 Xyleborus spec.

C: Isoptera:  
Coptotermes formosanus  
Cryptotermes brevis  
Heterotermes indicola  
10 Kalotermes flavicollis  
Mastotermes darwiniensis  
Reticulitermes flavipes  
Reticulitermes lucifugus  
Reticulitermes santonensis  
15 Zootermopsis nevadensis

Other active compounds which are suitable are algicides, molluscicides or active compounds against sea animals which colonise, for example, ship's bottom paints.

20 The following are particularly preferred as components in mixtures:

dichlofluanid, tolylfluanid,

benzyldimethyldodecylammonium chloride, didecyldimethyl-  
ammonium chloride,

tebuconazole, propiconazole, azaconazole, hexaconazole,

3-bromo-2,3-diiodo-2-propenyl alcohol, 3-iodo-2-propinyl  
n-butylcarbamate,

o-phenylphenol, m-phenylphenol, p-phenylphenol, 3-methyl-  
4-chlorophenyl,

5 thiocyanatomethylthiobenzothiazole,

N-methylisothiazolin-3-one, 5-chloro-N-methylisothia-  
zolin-3-one, 4,5-dichloro-N-octylisothiazolin-3-one,  
N-octyl-isothiazolin-3-one,

10 benzyl alcohol mono(poly)-hemiformal, N-methylolchloro-  
acetamide,

phoxim,

cyfluthrin, permethrin, cypermethrin, deltamethrin,  
imidacloprid.

15 The microbicidal compositions or concentrates used for  
the protection of industrial materials contain the active  
compound of the formula in a concentration from 0.01 to  
95 % by weight, in particular 0.01 to 60 % by weight, and  
additionally, if appropriate, 0.001 to 95 % by weight of  
one or more other suitable fungicides, insecticides or  
20 other active compounds as mentioned above.

The compositions according to the invention allow in an  
advantageous manner the microbicidal compositions avail-  
able to date to be replaced by more effective ones. They

have good stability properties and, advantageously, a broad spectrum of action.

Example 1

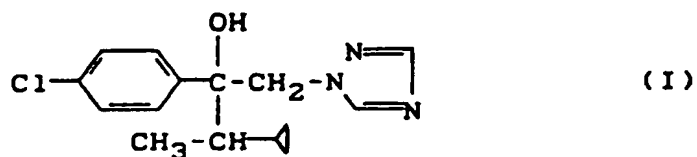
Inhibition test on giant colonies of Basidiomycetes

- 5 Mycelium sections were removed from colonies of  
Gloeophyllum trabeum, Coniophora puteana, Poria placenta,  
Lentinus tigrinus, Coriolus versicolor and Stereum  
sanguinolentum and incubated on an agar medium containing  
10 malt extract peptone at 26°C. The inhibition of hyphal  
growth on active-compound-containing media was compared  
with the longitudinal growth on media without an addition  
of active compound and rated as per cent inhibition.

At a concentration of 10 ppm, a 100 % inhibition is obtained with the compound cyproconazole.

### Patent Claims

1. Use of the compound of the formula (I)



- 5            its metal salts or acid addition compounds as a  
             microbicide for the protection of industrial  
             materials.
2. Use according to Claim 1, characterised in that the  
industrial material to be protected is wood or  
timber-derived products.
- 10          3. Microbicidal compositions for the protection of  
industrial materials, containing a compound of the  
formula (I) according to Claim 1 or its metal salts  
or acid addition compounds.
- 15          4. Composition according to Claim 3, characterised in  
that it contains, as an additional component, at  
least one other antimicrobially active compound,  
fungicide and/or other active compound for broaden-  
ing the spectrum of action or for achieving specific  
effects.
- 20          5. Compositions according to Claim 4, characterised in

that they contain at least one insecticide.

6. Method of protecting industrial materials, characterised in that the industrial materials are treated with a compound of the formula I according to Claim 1.

5

## Microbicidal Compositions

### A b s t r a c t

There are described the use of  $\alpha$ -(4-chlorophenyl)- $\alpha$ -(1-cyclopropylethyl)-1H-1,2,4-triazole-1-ethanol as a microbicide for the protection of industrial materials, and compositions containing this compound.